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Synthesis of Aluminum Nitride Nanowires from Carbon Nanotubes

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Aluminum nitride nanowires have been synthesized in bulk from carbon nanotubes (CNTs) at relatively low temperatures. This method produces AlN nanowires through the reaction of the carbon nanotubes, Al, and Al_2O_3 in a flowing NH_3 atmosphere. The diameters of the products, mainly in the range of 10−50 nm, correspond with the diameters of the carbon nanotubes, which provides a promising way to control the diameters of the AlN nanowires. The AlN nanowires fabricated in this way are single crystals covered by a thin amorphous layer. The small diameter and single crystal form make the AlN nanowires highly flexible. The growth mechanism of the AlN nanowires and the factors that allow a decrease in the synthesis temperature are discussed.

Introduction

Aluminum nitride (AlN) has many attractive properties, including high thermal conductivity, low coefficient of thermal expansion that closely matches that of silicon, high electrical resistivity, good mechanical strength, and excellent chemical stability. Thus it has attracted extensive interest for applications as electrical packaging material and as components in structural composites.[1] Meanwhile, AlN fibers and whiskers have recently attracted even more attention, as the perfect or near perfect crystal structure has a higher thermal conductivity (320 $W\cdot(m\cdot K)^{-1}$)[2] than ordinary polycrystalline AlN ceramics (30−260 $W\cdot(m\cdot K)^{-1}$),[2,3] and the fibers in the composites may exhibit better properties than powders do.[4,5] AlN powders or whiskers can be fabricated through a variety of methods. Two of the most extensively used methods in industry are carbothermal reduction and nitridation of α-alumina,[6,7] and direct nitridation of Al powders.[8−10] Because these methods require a reaction temperature of 1973−2073 K and $\geq$1773 K, respectively,[10] nanoscale Al particles are chosen, which can react with N_2 completely at 1173−1373 K.[8,9] To improve homogeneous mixing of carbon and alumina, the carbothermal reduction method has been modified by using aluminum metalorganic compounds instead of alumina as precursors.[11−13] The other two commonly used processes are self-propagating high-temperature combustion synthesis (SHS)[14,15] and microwave-assisted synthesis.[16,17] The former has many potential advantages such as low processing cost and high production, while the latter can fabricate AlN in a very short time with good energy efficiency. Besides the methods mentioned above, aerosol synthesis (or chemical vapor deposition)[18−20] and electrochemical synthesis[21] methods are also exploited for synthesis of AlN. Although ceramic nanowires are claimed to exhibit special properties,[22,23] hitherto AlN nanowires thinner than 50 nm have seldom been obtained in bulk.[8,9,15] Recently, a new process to synthesize nanowires based on templates was developed and was proved to be generally useful.[24−32] Based on a carbon nanotube

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(1) Kuramoto, N.; Taniguchi, H.; Aso, I. *Am. Ceram. Soc. Bull.* **1989**, *68*, 883.
(2) Sheppard, L. M. *Am. Ceram. Soc. Bull.* **1990**, *69*, 1801.
(3) Slack, G. A.; Mcnelly, T. F. *J. Cryst. Growth* **1976**, 34, 263.
(4) Zweben, C. *JOM* **1992**, *44* (7), 15.
(5) Zhang, Y. J.; Wang, Z. F.; Wang, N. L.; Jiang, G. S.; Lu, W. J.; Zhu, J. *Mater. Sci. Technol.* **1999**, *15*, 1225.
(6) Caceres, P. G.; Schmid, H. K. *J. Am. Ceram. Soc.* **1994**, *77*, 977.
(7) Corral, M. P.; Moreno, R.; Requena, J.; Moya, J. S.; Martinez, R. *J. Eur. Ceram. Soc.* **1991**, *8*, 229.
(8) Haber , J. A.; Gibbons, P. C.; Buhro, W. E. *J. Am. Chem. Soc.* **1997**, *119*, 5455.
(9) Haber , J. A.; Gibbons, P. C.; Buhro, W. E. *Chem. Mater.* **1998**, *10*, 4062.
(10) Selvaduray, G.; Sheet, L. *Mater. Sci. Technol.* **1993**, *9*, 463.
(11) Maya, L. *Adv. Ceram. Mater.* **1986**, *1*, 150.
(12) Stanley, D. R.; Birchall, J. D.; Hyland, J. N. K.; Thomas, L.; Hodgetts, K. *J. Mater. Chem.* **1992**, *2*, 149.
(13) Jung, W.-S.; Ahn, S.-K. *J. Mater. Chem.* **1994**, *4*, 949.
(14) Lee, W.-C.; Tu, C.-L.; Weng, C.-Y.; Chung, S.-L. *J. Mater. Res.* **1995**, *10*, 774.
(15) Jiang, G. J.; Zhuang, H. R.; Zhang, J.; Ruan, M. L.; Li, W. L.; Wu, F. Y.; Zhang, B. L. *J. Mater. Sci.* **2000**, *35*, 57 and 63.
(16) Ramech, P. D.; Rao, K. J. *Adv. Mater.* **1995**, *7*, 177.
(17) Vaidhyanathan, B.; Agrawal, D. K.; Roy, R. *J. Mater. Res.* **2000**, *15*, 974.
(18) Adjaottor, A. A.; Griffin, G. L. *J. Am. Ceram. Soc.* **1992**, *75*, 3209.
(19) Heymer, G.; Harnisch, H. U.S. Patent 3,352,637, 1967.
(20) Pratsinis, S. E.; Wang, G. Z.; Panda, S. *J. Mater. Res.* **1995**, *10*, 512.
(21) Travis, W.; Jongman, P.; Ernest, G. G.; Claudia, B. R.; Douglas, M. S.; Richard, M. C. *J. Am. Chem. Soc.* **1992**, *114*, 9457.
(22) Wong, E. W.; Sheehan, P. E.; Lieber, C. M. *Science* **1997**, *277*, 1971.
(23) Zhang, Y. J.; Wang, N. L.; He, R. R.; Zhang, Q.; Zhu, J.; Yan, Y. J.; *J. Mater. Res.* **2000**, *15*, 1048.
(24) Braun, P. V.; Osenar, P.; Stupp, S. I. *Nature* **1996**, *380*, 325.
(25) Li, Y.; Xu, D. S.; Zhang, Q. M.; Chen, D. P.; Huang, F. Z.; Xu, Y. J.; Guo, G. L.; Gu, Z. N. *Chem. Mater.* **1999**, *11*, 3433.
(26) Dai, H. J.; Wong. E. W.; Lu, Y. Z.; Fan, S. S.; Lieber, C. M. *Nature* **1995**, *375*, 769.
(27) Han, W. Q.; Fan, S. S.; Li. Q. Q.; Hu, Y. D. *Science* **1997**, *277*, 1287.
(28) Zhang, Y. J.; Zhu, J.; Zhang, Q.; Yan, Y. J.; Wang, N. L.; Zhang. X. *Chem. Phys. Lett.* **2000**, *317*, 504.

10.1021/cm001422a CCC: $20.00

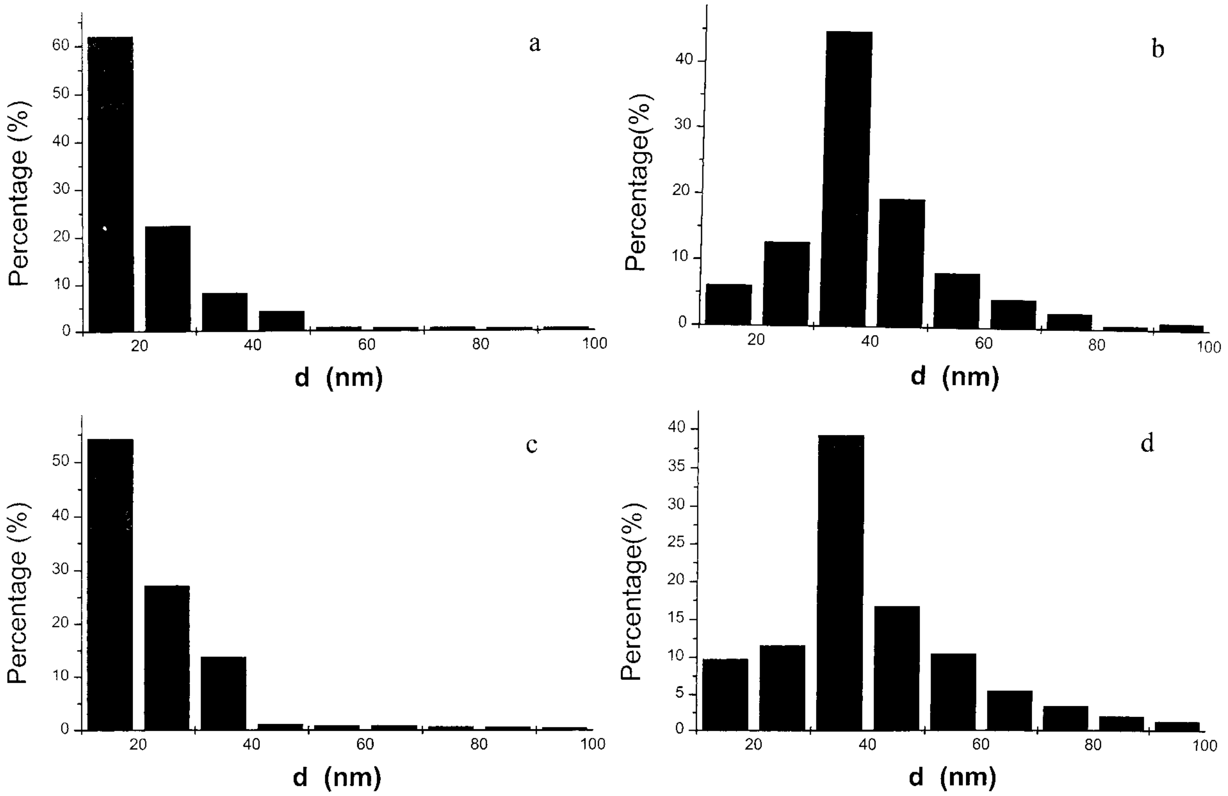

Figure 1. Size histogram for (a) the thin CNTs, (b) the thick CNTs, (c) the thin AlN nanowires fabricated by using the thin CNTs, and (d) the thick AlN nanowires fabricated by using the thick CNTs.

Table 1. Synthesis Conditions of the AlN Nanowires[a]

no.	Al	Al_2O_3	NH_3	N_2	Al_2O_3 tube	stainless steel tube	av diam (nm) of CNTs	reacn temp(K)
1	+	+	+		+		15	1223
2	+	+	+		+		15 or 35	1273−1623
3	+	+	+		+		15	1773
4	+	+		+	+		15	1373−1573
5	+		+		+		15	1473−1573
6		+	+		+		15	1473−1773
7	+		+			+	15	1473−1673
8*	+		+			+	15	1473−1673
9	+	+	+				absent	1273−1573

[a] Notes: + denotes which is used in this experiment; * denotes that a little O_2 is introduced.

confined reaction or a substitution reaction, several kinds of nanowires have been fabricated.[26−32] The aim of the present work is to fabricate AlN nanowires in bulk with small diameters, especially in 10−50 nm range at relatively low cost, using the carbon nanotube confined reaction method.

Experimental Section

The experimental system used for producing AlN nanowires is similar to the one reported previously.[27] Solid reactants, commercial Al_2O_3 powders (−200 mesh, i.e., less than 74 μm in size) or Al powders (−200 mesh) or mixture of both (1:1 in weight) were placed in a ceramic boat and then covered by carbon nanotubes (CNTs). On top of the CNTs, another thin layer of the reactants mentioned above covered the CNT layer. The amounts of the solids reactants (Al, Al_2O_3) are more than the needs according to the reactions of Al (Al_2O_3) and the CNTs. The ceramic boat was placed in an alumina tube or a stainless steel tube placed in a conventional horizontal furnace. Two kinds of CNTs were prepared by an improved floating catalyst method.[33] The CNTs produced by this method are high in purity, and all of them are MWCNTs. The diameters of the CNTs were not absolutely uniform. Statistical counting of more than 1500 nanotubes revealed that the average diameters of the two kinds of CNTs were about 15 nm (thin CNTs) and 35 nm (thick CNTs), respectively, and the detailed diameter distributions for them are shown in Figure 1. NH_3 or N_2 were used as reactant gas respectively, and their flow rates were 300−500 cm^3(STP) min^{-1}. Compared with the traditional carbothermal reduction method, the AlN nanowires were fabricated at a relatively low temperature of 1223−1473 K for a shorter time of 1 h. Different synthesis conditions (listed in Table 1) were used so that the synthesis parameters could be optimized.

After the reactions, the black CNTs turned into a gray product. The morphology and atomic structure of the product were characterized by using a scanning electron microscope

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(29) Tang, C. C.; Fan, S. S.; Dang, H. Y.; Zhao, J. H.; Zhang, C.; Li, P.; Gu, Q. *J. Crystal. Growth* **2000**, *210*, 595.

(30) Han, W. Q.; Bando, Y.; Kurashima, K.; Sato, T. *Appl. Phys. Lett.* **1998**, *73*, 3085.

(31) Han, W.; Philipp, K.-R., Frank, E.; Manfred, M. *Chem. Mater.* **1999**, *11*, 3620.

(32) Han, W. Q.; Fan, S. S.; Li, Q. Q.; Liang, W. J., Gu, B. L.; Yu, D. P. *Chem. Phys. Lett.* **1997**, *265*, 374.

(33) Cheng, H. M.; Li, F.; Su, G.; Pan, H. Y.; He, L. L.; Sun, X.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1998**, *72*, 3282.

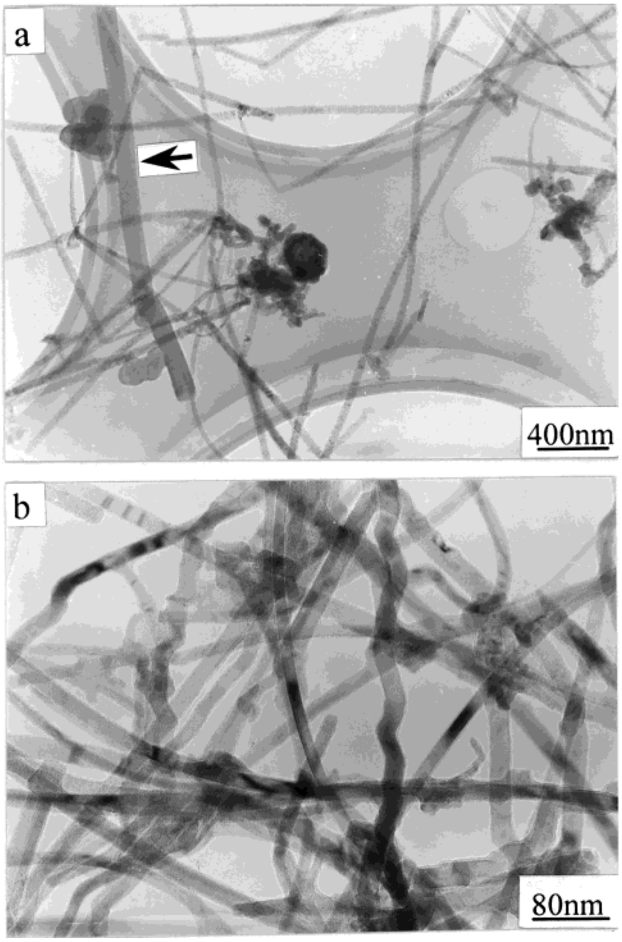

Figure 2. AlN nanowires synthesized by using the carbon nanotubes with different average diameters: (a) 35 nm; (b) 15 nm. A thick CNT (>100 nm) remains unchanged after reaction (marked by an arrow).

(SEM, JEM-6301F) and a filed-emission gun transmission electron microscope (TEM, JEM-2010F). The TEM was equipped with an energy dispersive spectrometer (EDS) and an electron energy loss spectrometer (EELS).

Results

No crystalline nanowires are found until the reaction temperature is raised to 1223 K (experiment 1). However, at this reaction temperature, only a small percentage of CNTs (less than 20%) are turned into crystalline AlN nanowires. Fabrication of a higher percentage (more than 95%) of AlN nanowires requires a higher temperature (experiment 2). The products in this experiment are mainly nanowires with a high aspect ratio (length/diameter); their lengths range from several micrometers to hundreds of micrometers. When carbon nanotubes of 35 nm in average diameter are used as the reactants, thick AlN nanowires of 35−40 nm in average diameter are fabricated, while thinner AlN nanowires of 15−20 nm in average diameter are obtained when the carbon nanotubes of 15 nm in average diameter are used (Figure 2). Due to the difference in the diameter of the CNTs, the diameters of the AlN nanowires are not very uniform. Some AlN nanowires have diameters very much different from their average diameter. In addition, some CNTs (marked by an arrow in Figure 2) have larger diameters (>100 nm) and they remain unchanged after the reaction. The detailed diameter distribution of the AlN nanowires (also through statistical counting) fabricated from the CNTs with different average diameters is shown in Figure 1. It is found that the diameter distributions of the AlN nanowires are fairly similar to those of the CNTs. Most of the thin AlN nanowires (Figure 1c) and CNTs (Figure 1a) are less than 30 nm in diameter, while most of the thick AlN nanowires (Figure 1d) and CNTs (Figure 1b) range from 20 to 50 nm in diameter, especially in the range of 30−40 nm. Despite the existence of a slight difference in the diameter distribution of the AlN nanowires and the CNTs, our results clearly show a direct proportional relationship between the diameters of the AlN nanowires and those of the CNTs. The template effect of the CNTs on the growth of the AlN nanowires is distinct. This template effect works at a wide range of reaction temperatures and times. At temperatures less than 1623 K and in reaction times ranging from 30 to 200 min, the AlN nanowires have similar diameter distribution as shown in Figure 1. Thus by changing the reactant carbon nanotubes, we can control the diameters of the products. Since bulk fabrication of highly arranged carbon nanotubes with certain diameters is not difficult,[34,35] the above method would be a new and effective way to control the diameter of the nanowire. However, when the reaction temperature is raised to 1773 K, the nanowires are coarsened significantly as shown in Figure 3. The diameters of the AlN fibers fabricated at 1773 K are usually larger than 100 nm or several hundreds of nanometers. In addition, some of these AlN nanowires have low aspect ratio and anomalous shapes. In some cases, the diameter along the axis of the AlN fiber seems very uneven (Figure 3b). This implies that the template effect of the CNTs does not work well and some of the AlN fibers may grow in a way similar to that of the nitridation of Al powders at this high temperature.[8−10]

High-resolution electron microscopy (HREM) provides structural details of the AlN nanowires. Figure 4a shows an HREM image of a single AlN nanowire with a diameter of about 10 nm. The nanowire is a good single crystal coated with an amorphous layer. EELS of this AlN nanowire is shown in Figure 5a. From the left to the right, the peaks correspond to the Al−$L_{2,3}$, N−K, and O−K peaks, respectively, and their positions and shapes are in good agreement with the reported results.[6,36] It is noted that AlN nanowires with a relatively thicker amorphous layer (The thickness of the layer is lager than 1 nm, and the ratio of the diameter of the crystalline core to the diameter of the nanowires is usually larger than 0.7:1.) are seldom found. In most cases, the typical nanowires usually have a very thin (<1 nm) or intermittent amorphous layer. The HREM image of the typical AlN nanowire is shown in Figure 4b. In some cases, there are stacking faults in the nanowires. The selected area electron diffraction (SAED) in Figure 4 and a serial of other SAED show that our nanowires are of the hexagonal wurtzite type AlN with

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(34) Li, W. Z.; Xie, S. S.; Qian, L. X.; Chang, B. H.; Zou, B. S.; Zhou, W. Y.; Zhao, R. A.; Wang, G. *Science* **1996**, *274*, 1701.

(35) Fan. S. S.; Chapline, M. G.; Franklin, N. R.; Tombler, T. W.; Cassell, A. M.; Dai, H. *Science* **1999**, *283*, 512.

(36) Ahn, C. C.; Krivanek, O. L.; Burgner, R. P.; Disko, M. M.; Swann, P. R. *EELS Atlas*, a joint project of the ASU HREM facility and GATAN: Warrendale, PA and Tempe, AZ, 1983.

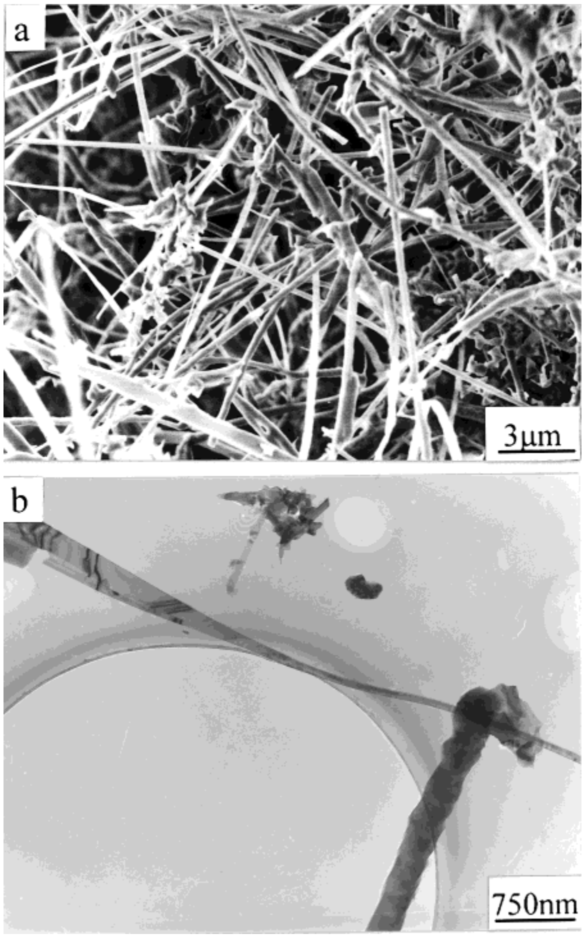

Figure 3. AlN nanowires (fibers) synthesized at 1773 K: (a) SEM micrograph showing morphology of the fibers; (b) TEM micrograph showing an AlN fiber with uneven diameter along its axis.

lattice parameters of $a = 0.311$ nm and $c = 0.498$ nm. The growth directions of the AlN nanowires (in Figure 4) are all normal to one of the {10·0} crystal planes, which is consistent with other works.[37,38] Compared with the EELS in Figure 5a, the O peak of the EELS in Figure 5b of the nanowire with a very thin (or absent) amorphous layer is much lower and O is present in grounds below the detection limits. Considering the precision of quantitative EELS in our TEM, the oxygen content in this kind of AlN nanowires is less than 1%. Since there is usually an amorphous layer of metal or nonmetal oxide covering on the other nanowires synthesized by the CNTs-confined method, we believe that the amorphous layer is a compound of Al and O, which results in a higher O peak of the EELS in Figure 5a. The content of O in the AlN nanowires changes corresponding to the thickness of the amorphous layer and ranges from 5 to 30 at. %. If the component of the amorphous layer is supposed to be Al_2O_3, then the atomic ratios of the Al and N in the crystalline cores are calculated as about 0.95−1.05. Meanwhile the ratios of the Al and N in the nanowires with a very thin (or absent) amorphous layer are about 0.97−1.03. Thus, the nanowires in the present work are stoichiometric AlN nanowires.

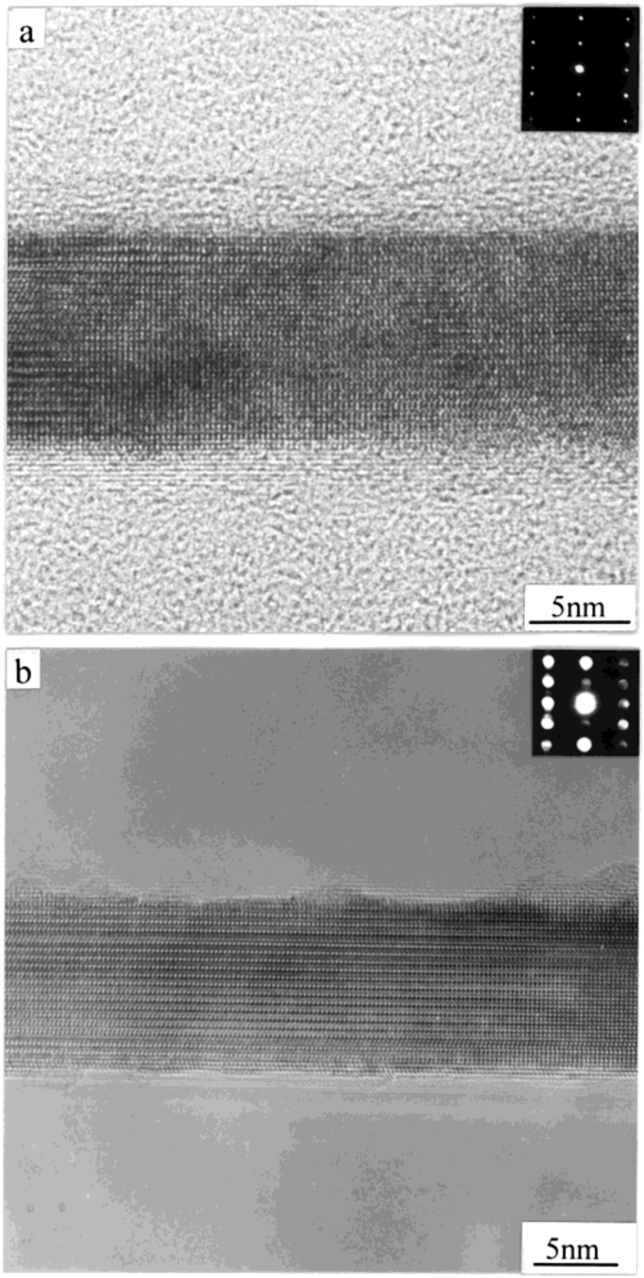

Figure 4. HREM image of an AlN nanowire (a) with a thick amorphous layer and (b) with a very thin amorphous layer.

Similar to carbon nanotubes,[39−41] these single-crystal nanowires show good flexibility and high bending strength.[22,23] Under illumination of the electron beam with varying current density in TEM, reproducible bending of the AlN nanowires is also observed. An AlN nanowire is in its original position when the current density is small (Figure 6a), while the nanowire bends to an angle about 45° at a higher current density (Figure 6b). If this higher current density is reduced to a small enough value, the nanowire reverts back to its original position again. As the bending can be varied continu-

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(37) Drum, C. M.; Mitchell, J. M. *Appl. Phys. Lett.* **1964**, *4*, 164.

(38) Zhou, H. P., Chen, H.; Wu, Y.; Miao, W. G.; Liu, X. *J. Mater. Sci.*, **1998**, *33*, 4249.

(39) Knechtel, W. H.; Düsberg, G. S.; Blau, W. J.; Hernández, E.; Rubio, A. *Appl. Phys. Lett.* **1998**, *73*, 1961.

(40) Poncharal, P.; Wang, Z. L.; Ugarte, D.; Heer, W. A. *Science* **1999**, *283*, 1513.

(41) Falvo, M. R.; Clary, G. J.; Taylor, R. M.; Chi, V.; Brooks, F. P., Jr.; Washburn, S.; Superfine, R. *Nature* **1997**, *389*, 582.

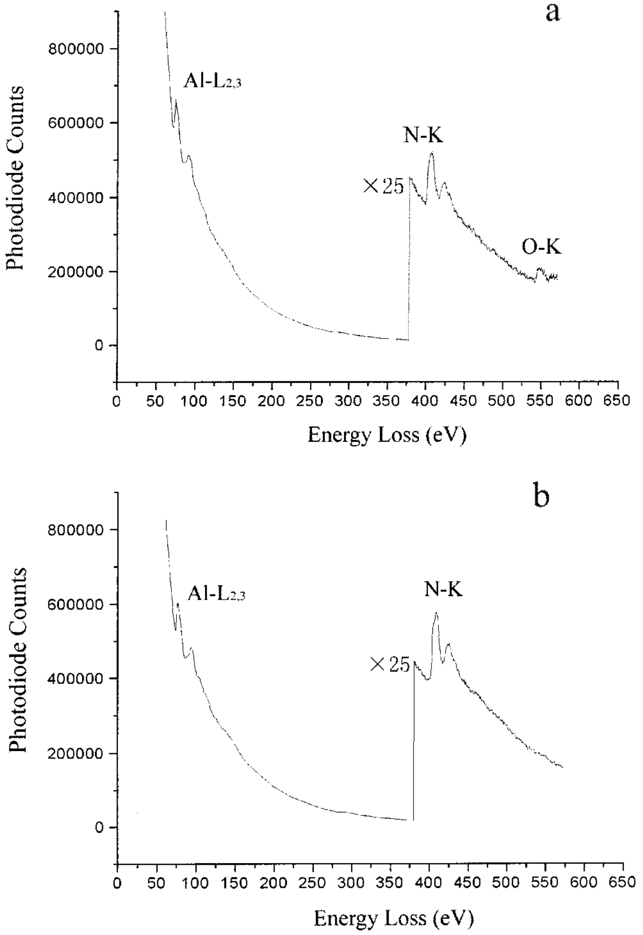

Figure 5. EELS spectra of an individual AlN nanowire (a) with a thick amorphous layer and (b) with a very thin amorphous layer.

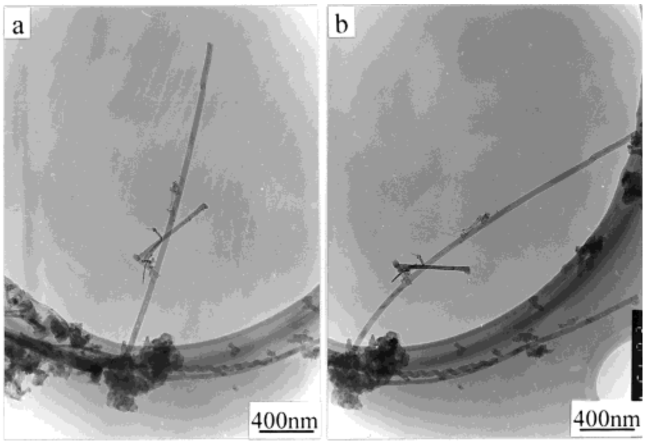

Figure 6. Bending of an AlN nanowire in an electron beam (a) in its original position and (b) bent to the right.

ously, it is highly reproducible and exhibits spring-like behavior; we assume that few defects are introduced by the bending. The good single-crystal structure and the good flexibility of the AlN nanowire would benefit its application as components of ceramic or alloy composites.

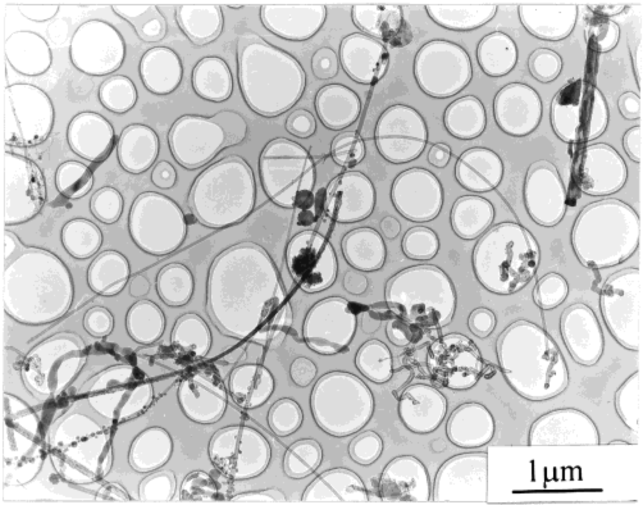

Figure 7. Morphology of the products obtained when O_2 is introduced but raw Al_2O_3 powders are absent.

Experiments 4−7 and experiment 9 show that Al, NH_3, and Al_2O_3 are all important to synthesize the AlN nanowires. When CNTs are absent in experiment 9, no whiskers (or nanowires) but particles are found in the products. The diameters of the particles range from 100 nm to several tens of micrometers but are mainly larger than 10 μm. EDS shows that the compositions of the particles are mainly Al and N or Al and O, respectively. The precursors of the former particles may be the Al powders, which react with NH_3 and produce AlN. The precursors of the latter particles may be Al_2O_3. Al_2O_3 powders do not react with NH_3 greatly; thus, only a small amount of AlN deposits on the Al_2O_3 particles. When Al is absent in experiment 6, no AlN nanowires are found. When NH_3 is substituted by N_2 in experiment 4, no AlN nanowires are fabricated until the temperature is raised to 1373 K. When the Al_2O_3 powders (raw reactant) are absent but an Al_2O_3 tube and Al_2O_3 boat are used (experiment 5), the yield of the AlN nanowires is small compared with that in experiment 2. Moreover, when a stainless steel tube and BN boat are used instead of the Al_2O_3 tube and the Al_2O_3 boat, respectively, and the Al_2O_3 powders are also absent (experiment 7), only a very small quantity of the AlN nanowires can be found. Experiment 8 provides a new way to synthesize the AlN nanowires when other reaction conditions in experiment 7 are maintained. The new method is to introduce a little O_2 (1−5 vol %) into the NH_3 flow. As shown in Figure 7, there are nanowires, hollow crystalline nanotubes, CNTs, and CNTs covered by crystalline powders in the product. The nanowires can be identified as AlN nanowires. The results of experiments 5, 7, and 8 reveal that Al_2O_3 and O_2 have a somewhat similar effect in the growth of the AlN nanowires in the present work.

Discussion

In analogous efforts to grow GaN nanowires,[27] Ga_2O was concluded to be produced first through the following reaction at 1173 K,

$$4Ga(s) + Ga_2O_3(s) \rightarrow 3Ga_2O(g) \qquad (1)$$

However, Al_2O is difficult to obtain at low temperature (for example, 1400 K) because it is hard to reduce Al_2O_3 by Al or carbon due to the high positive change of Gibbs free energy ΔG for the following reactions:[42]

$$Al_2O_3(s) + 2C(s) \rightarrow Al_2O(g) + 2CO \quad \Delta G = 519.54 \text{ kJ/mol} \quad (2)$$

$$Al_2O_3(s) + 4Al(s) \rightarrow 3Al_2O(g) \quad \Delta G = 512.64 \text{ kJ/mol} \quad (3)$$

Meanwhile, Al and NH_3 (or N_2) may react with each other even at 1173 K,[8,9] and this is a highly exothermic reaction ($\Delta G = -547.2$kJ/mol).[42]

$$2Al(s) + 2NH_3 \rightarrow 2AlN(s) + 3H_2 \quad (4)$$

We assume that this highly exothermic reaction may result in local high temperatures in some small areas. This high temperature may promote reaction 2 or 3; thus the AlN nanowires are produced according to the following reactions:

$$2Al_2O(g) + C(s) + 4NH_3 \rightarrow 4AlN(s) + CO + 5H_2 + H_2O(g) \quad (5)$$

Therefore, we assume that the AlN nanowires are fabricated by two independent reactions. One is the exothermic reaction of Al and NH_3 (reaction 4), which provides heat to promote the reduction of the Al_2O_3 by carbon or aluminum. The other is the growth of the AlN nanowires in the areas confined by the CNTs (reaction 5).

The growth mechanism can explain the importance of the CNTs, Al, and Al_2O_3 in the reaction. CNTs act as the template and play a key role to control the size of the AlN nanowires. If the CNTs are absent, only powders are fabricated as mentioned above. Besides serving as the raw material for the fabrication of the AlN nanowires, the Al_2O_3 powders act as oxidizers to oxidize carbon. In an ideal CNTs−Al−NH_3–AlN system without oxygen, the CNTs would probably keep their original forms and no AlN nanowires would be fabricated. However, existence of a small amount of oxygen in the present synthesis system is unavoidable, especially for the Al_2O_3 tube due to the micropores on it. Al and O react slowly and produce $Al_2O_3(g)$. The newly produced $Al_2O_3(g)$ can be used to fabricate a small quantity of AlN nanowires when the Al_2O_3 is not introduced as the reactant in experiment 5. If O_2 is added into the reaction chamber (the stainless steel tube) as in experiment 8, the added O_2 reacts with Al vapor and produces enough $Al_2O_3(g)$ to synthesize the AlN nanowires. Consequently, more AlN nanowires are fabricated in experiment 8 than in experiment 5. On the other hand, when a stainless steel tube is used to replace the Al_2O_3 tube in experiment 7, less O_2 can enter into the reaction chamber and much fewer AlN nanowires are fabricated.

Al acts as not only the raw material to produce AlN, but also a thermal energy source to promote the reaction of Al_2O_3 with other reactants. However, the heat produced by the reaction 4 is limited to a small area, and reactions 2 and 3 are relatively difficult to carry out; thus the yield of the Al_2O is small. In similar work to synthesize SiC nanowires,[26,29,31,32] three reactions are believed to occur:

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO \quad (6)$$

$$SiO(g) + 2CO \rightarrow SiC(s) + CO_2 \quad (7)$$

$$C(s) + CO_2 \rightarrow 2CO \quad (8)$$

Reaction 6 is the main reaction. The byproduct CO gas in this reaction increases or decreases the diameters of the SiC nanowires through reaction 7 or 8. A newly developed method[29] to synthesize SiC nanowires with selected diameters is to put the CNTs in the downstream of the gas flow and to carry away CO gas rapidly by Ar gas so that reactions 7 and 8 are greatly suppressed. As mentioned above, the byproduct CO and the intermediate product Al_2O in our work are less. Therefore, the existence of little byproduct and intermediate product cannot greatly change the diameters of the AlN nanowires and the CNTs show a good template effect. However, at high reaction temperatures, for example, 1773 K, Al and NH_3 may grow into the AlN fibers directly and these fibers usually have larger diameters.[10,11,43]

In the present work, the AlN nanowires start to grow at 1223 K. The relatively low starting growth temperature can be ascribed to the exothermic reaction of Al and NH_3, using NH_3 as the reactant gas, and the large surface area of the carbon nanotubes. As stated above, the nitridation of Al is a highly exothermic reaction, which may be one of the reasons for the growth of the AlN nanowires at low temperatures. When NH_3 is used, the reaction temperature can be decreased by 200 K,[43] which might be due to the formation of reactive atomic nitrogen.[44] In contrast, in the experiments using N_2, even at 1373 K, only a few imperfect AlN nanowires were fabricated. Meanwhile, the high specific surface area of the carbon nanotubes may promote the reaction between Al_2O and carbon, which is supposed to be analogous to the role of nanoscale Al powders,[7,8] and therefore decreases the nitridation temperature. In fact, as mentioned above, the carbon nanotube (marked by an arrow in Figure 2) with a larger diameter (>100 nm) remains unchanged after the reaction, while other carbon nanotubes with smaller diameters turn into AlN nanowires.

Conclusion

In summary, a carbon nanotube confined reaction has been employed to synthesize AlN nanowires in bulk at 1223−1473 K. These AlN nanowires, whose diameters are mainly in the range of 10−50 nm and directly correlated with those of the carbon nanotubes, are among the thinnest ones known. The nanowires are good single crystals and show great flexibility, which may be useful when these nanowires are used as components of ceramic or alloy composites. Due to the low synthesis temperature and use of the cheap commercial reactants of Al and Al_2O_3 powders, the method

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(42) Liang, Y. J.; Che, M. X. *Handbook for thermodynamic data of inorganic compounds*; Press of Northeast University: Shenyang, China, 1993.

(43) Kimura, I.; Ichiya, K.; Ishii, M.; Hotta, N.; Kitamura, T. *J. Mater. Sci. Lett.* **1989**, *8*, 303.

(44) Bradshaw, S. M.; Spicer, J. L. *J. Am. Ceram. Soc.* **1999**, *82*, 2293.

should be suitable for the synthesis of thin single crystal AlN nanowires for various applications. The growth mechanism of the AlN nanowires is analyzed, and it is proposed that the exothermal nitridation of the Al may promote the growth of the AlN nanowires through the CNTs-confined reaction. The relatively low reaction temperature compared with the traditional carbothermic reduction may be attributed to the use of NH_3, the high specific surface area of the carbon nanotubes and the exothermic reaction of the Al and NH_3.

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